Doping of thiolate protected gold clusters through reaction with metal surfaces

KAZAN, Rania, MUELLER, Ulrich Patrick, BUERGI, Thomas

Abstract

A new technique is introduced for doping gold nanoclusters by using a metal surface such as Ag, Cu and Cd as a source of heteroatoms. The importance of the thiol ligand in the doping process is examined by following the reactions with MALDI-TOF mass spectrometry in the presence and the absence of the thiols on the surface. The doping reactions depend greatly on the type of the cluster and the availability of the ligand which is a crucial element for alloying. The thiol acts as a messenger exchanging the metal atoms between the cluster and the metal surface as revealed by the XPS studies performed on the metal surfaces.

Reference

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Doping of Thiolate Protected Gold Clusters through Reaction with Metal Surfaces

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Figure S1. MALDI mass spectra of the pure Au\(_{38}\)(2-PET)\(_{24}\) (a) and Au\(_{25}\)(2-PET)\(_{18}\) (b) nanoclusters respectively. The peaks marked with an asterisk correspond to the different fragments of the clusters.
**Estimation of cluster amount needed**

The amount of gold nanoclusters need for the reactions was chosen such that it equals the number of thiolate molecules covering the foil. The latter number was estimated from the known macroscopic surface area by assuming a (111) surface and a c (4 × 2) superlattice structure of the adsorbed thiolutes (four thiolutes per unit cell).

\[
N_{\text{gold nanoclusters}} = N_{\text{thiolate molecules on the surface}} \quad (1)
\]

The number of thiolate molecules covering the foil’s surface can be calculated as follows:

\[
N_{\text{thiolate molecules/cm}^2} = \frac{N_{\text{thiolate molecules in one unit cell}}}{\text{area of the unit cell}} = \frac{4 \text{ molecules}}{0.866 \times 10^{-14} \text{ cm}^2} = 4.62 \times 10^{14} \text{ molecules/cm}^2 \quad (2)
\]

\[
\text{Area of unit cell} = a \times b = 10 \text{ Å} \times 8.66 \text{ Å} = 86.6 \text{ Å}^2 = 0.866 \times 10^{-14} \text{ cm}^2 \quad (3)
\]

Taking into account that the foil’s surface area is set to around two cm² in all the experiments, one can calculate the number of thiolate molecules covering the surface and hence the corresponding number of clusters involved in the reaction.

**In the case of the Au_{25}(2-PET)_{18} cluster for example:**

\[
N_{\text{Au}25 \text{ nanoclusters}} = N_{\text{thiolate molecules}} = 9.24 \times 10^{14} \text{ cluster (for 2 cm}^2 \text{ foil}).
\]

\[
n_{\text{Au}25} = 1.53 \times 10^{-9} \text{ mol} = 1.53 \text{ nmol}
\]

Nevertheless, in the reaction of the Au_{25} nanocluster with the Cu-2PET modified surface, a total instantaneous (within 2 minutes) decomposition of the cluster was observed when using the exact amount of Au_{25} required (Figure S3). This can be attributed to the instability of the heavily copper doped clusters. Therefore, the reaction was performed by doubling the amount of the cluster needed.
Figure S3. MALDI mass spectrum of the sample taken after two minutes during the reaction of the Au$_{25}$(2-PET)$_{18}$ with the Cu surface modified by 2PET.

Table S1. Variation in the number of gold atoms exchanged and the number of gold monolayers deposited on the surface of the silver foil during the reaction of Au$_{25}$ nanocluster with Ag surface modified by 2PET.

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>$\bar{x}$</th>
<th>N of Au atoms exchanged ($10^{14}$)</th>
<th>N of Au Monolayers</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.9913</td>
<td>9.1214</td>
<td>0.3317</td>
</tr>
<tr>
<td>60</td>
<td>1.4624</td>
<td>13.4558</td>
<td>0.4894</td>
</tr>
<tr>
<td>180</td>
<td>2.3496</td>
<td>21.6190</td>
<td>0.7863</td>
</tr>
<tr>
<td>300</td>
<td>3.0247</td>
<td>27.8303</td>
<td>1.0122</td>
</tr>
<tr>
<td>480</td>
<td>3.5329</td>
<td>32.5067</td>
<td>1.1823</td>
</tr>
<tr>
<td>1500</td>
<td>4.9766</td>
<td>45.7901</td>
<td>1.6655</td>
</tr>
</tbody>
</table>

Where:

\[
\begin{align*}
N_{\text{Au atoms exchanged}} &= \bar{x} \times nb\ of\ gold\ nanocluster\ reacting\ \text{(eqt. 1)} \quad (4) \\
N_{\text{Ag atoms on the surface}} &= \text{Area of the foil} \times N_{\text{Ag atoms on Ag (111) surface}} \times \text{surface area} \quad (5) \\
N_{\text{Au monolayers deposited on foil surface}} &= \frac{N_{\text{Au atoms exchanged}}}{N_{\text{Ag atoms on surface}}} \quad (6)
\end{align*}
\]

\[N_{\text{Ag atoms on Ag (111) surface}} = 13.8 \times 10^{14} \text{ atoms/cm}^2\] and Area of the foil = 1.99 cm$^2$
Figure S4. MALDI mass spectrum of Au$_{25-x}$Cu$_x$(2-PET)$_{24}$ doped nanoclusters. Number of copper atoms incorporated is marked in red above the corresponding peaks. The peaks marked with a blue correspond to the loss of a Cu atom from each of the doped species. The peaks marked with a green asterisk correspond to the loss of a S atom from the doped species and the fragments (marked in blue) respectively. The sample was taken at one hour reaction time.

Figure S5. MALDI mass spectra of the samples taken at different times during the reaction of Cu surface (no pre-adsorbed thiol) with Au$_{25}$(2-PET)$_{18}$ (a) and Au$_{38}$(2-PET)$_{24}$ nanoclusters (b) respectively.
Figure S6. MALDI mass spectra of the samples taken at different times during the reaction of the Cd surface (no pre-adsorbed thiol) with Au$_{25}$(2-PET)$_{18}$ (a) and Au$_{38}$(2-PET)$_{24}$ (b) nanoclusters, respectively.

Figure S7. MALDI mass spectra of the samples taken simultaneously with the studied foils at different times during the reaction of Au$_{25}$(2-PET)$_{18}$ nanocluster with the Ag foil modified by 2-PET. The number of doped Ag atoms is marked in black above the corresponding peak and it is noticed that the doping herein is slower than before due to the gradual removal of the foil pieces from the reaction mixture.
Figure S8. (a) Variation in the [Au]/([Au]+[Ag]) ratio on the surface of the silver foils removed at different reaction times during the reaction between $\text{Au}_{25}(2\text{-PET})_{18}$ nanocluster with the Ag foil modified by 2-PET. (b) Variation in the average number of doped Ag atoms ($\bar{x}$) during the reaction as obtained from the MALDI mass spectra in figure S7.

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>[S]/[Ag] (%)</th>
</tr>
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<tbody>
<tr>
<td>60</td>
<td>7.84</td>
</tr>
<tr>
<td>180</td>
<td>5.63</td>
</tr>
<tr>
<td>300</td>
<td>8.1</td>
</tr>
<tr>
<td>1080</td>
<td>12.44</td>
</tr>
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</table>

Table S2. Variation in the [S]/[Ag] ratio (%) on the surface during the reaction of $\text{Au}_{25}(2\text{-PET})_{18}$ nanocluster with the Ag foil modified by 2-PET. The sulphur/silver atomic concentration ratio (%) on the reference foil is 9.14%.

Figure S9. (a) MALDI mass spectra of the samples taken (simultaneously with the studied foils) at different times during the reaction of $\text{Au}_{25}(2\text{-PET})_{18}$ nanocluster with the 2-PET free Ag-foil. The number of doped Ag atoms is marked in black above the corresponding peak. (b) Zoom in of the mass spectrum in the range 6750 - 7430 Da with the clear peaks of the different $\text{Au}_{25}/\text{Ag}_x$ alloys formed.
Figure S10. (a) Variation in the [Au]/([Au]+[Ag]) ratio on the surface of the silver foils removed at different reaction times during the reaction between Au$_{25}$(2-PET)$_{18}$ nanocluster with the 2-PET free Ag-surface. (b) Variation in the average number of doped Ag atoms ($\bar{x}$) during the reaction as obtained from the MALDI mass spectra in Figure S9.

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>[S]/[Ag] (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>9.11</td>
</tr>
<tr>
<td>300</td>
<td>2.57</td>
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<tr>
<td>480</td>
<td>5.39</td>
</tr>
<tr>
<td>1440</td>
<td>3.66</td>
</tr>
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Table S3. Variation in the [S]/[Ag] ratio (%) on the surface during the reaction of Au$_{25}$(2-PET)$_{18}$ nanocluster with the 2-PET free Ag-foil.

Figure S11. MALDI mass spectra of the samples taken together with the studied foils at different times during the reaction of Au$_{25}$(2-PET)$_{18}$ nanocluster with the 2-PET modified Cu surface (a) and 2-PET free Cu surface (b) respectively. From right to left, the dashed line marks the peak corresponding to the incorporation of an extra copper atom (a). Peaks marked with an asterisk correspond to the loss of an Au-L unit (b).
Figure S12. XPS spectra of the copper substrates taken at different times during the reaction of the Au$_{25}$(2-PET)$_{18}$ nanocluster with the 2-PET modified Cu foil (a) and Cu foil (without pre-adsorbed 2-PET) (b). The black spectra correspond to the reference unreacted Cu foils modified by 2-PET (a), and 2-PET free (b) respectively.